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HYPERFINE SPLITTINGS IN THE NEAR-INFRARED SPECTRUM OF $^{14}NH_3$

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Sub-Doppler, saturation dip, measurements of transitions in the $\nu_1 + \nu_3$ band of $^{14}NH_3$ have been made by frequency comb-referenced diode laser absorption spectroscopy. The observed spectra exhibit either resolved or partially-resolved hyperfine splittings that are primarily determined by the ^{14}N quadrupole coupling in the molecule. Modeling of the line shapes based on the known hyperfine level structure of the ground state of the molecule shows that, in nearly all cases, the upper state level has splittings similar to that of the same rotational level in the ground state. The data provide accurate frequencies for the line positions and the observed hyperfine splittings can be used to make or confirm rotational assignments. Of all the measurements, one transition, $^pP(5,4)_a$ at 195 994.73457 GHz, exhibits hyperfine structure which does not conform to that expected based on extrapolation from the known lower state hyperfine splittings. Examination of the known vibration-rotation level structure near the upper state energy shows that there exists a near degeneracy between this level and one in the $\nu_1 + 2\nu_4$ manifold which is of the appropriate symmetry to be mixed by magnetic hyperfine terms that couple ortho- and para- modifications of the molecule. It is possible that the unusual hyperfine splittings are a consequence of ortho-paro mixing, which has been predicted, but not previously seen in ammonia and further experimental measurements to investigate this possibility are ongoing.

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